

# DESIGN OF MULTI-STAGE LIQUEFACTION PROCESS FOR COMPLETE COAL CONVERSION AND EXTENSIVE UPGRADING

Isao Mochida, Kinya Sakanishi, Masahiro Kishino, Katsuyuki Honda  
Institute of Advanced Material Study, Kyushu University,  
Kasuga, Fukuoka 816, JAPAN

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## INTRODUCTION

Increasing coal consumption to meet the increasing demand of energy in the world should minimize the effects on the environment on the earth. The highest efficiency of energy use and the deepest reduction of pollutants such as SO<sub>x</sub>, NO<sub>x</sub> and solid waste are the key technologies to solve the problems of climate change, acid rain and environmental contamination urgently to prepare their rapid growth. Thus, clean coal technologies are most expected to be developed. The ultimate cleaning of coal can be achieved only after the complete conversion of coal into fluid form by removing completely the pollutant sources of S, N and minerals since they are bound intimately to the organic parts.

The liquefaction has been proved to provide the whole products to be completely free from pollutants and very handy for clean uses. The problems still remain in the low efficiency and high cost. Hence, the authors set up the targets of the current liquefaction technology.<sup>1)</sup>

1. Complete conversion of coal organics into fluid fuels, leaving only minerals to be fully separated in forms free from contaminants.

2. Catalyst recovery from minerals to recycle it and reduce the amount of solid wastes.

To achieve the targets, authors are examining;

1. Coal pretreatment to enhance its reactivity through removal of minerals and oxygen functional groups as well as reagent impregnation.<sup>2,3)</sup> The problems of scale and sludge are expected to be moderated.<sup>4)</sup>

2. Design of hydrogen donor and dissolving solvents.<sup>5,6)</sup>

3. Rapid heating and short contact time at a fairly high temperature for the hydrogen transferring liquefaction.<sup>7,8)</sup>

4. Design of recoverable catalysts of high activity<sup>9)</sup>

The suppression of preasphaltene formation by controlling retrogressive reactions during the liquefaction, or its activation and digestion if it is produced, and the modification of less reactive components including some of inert macerals are the key objectives in our current study.

## EXPERIMENTAL

An Australian subbituminous (Wandoan) coal, its liquefaction residue (WD-LR) in a 1 t/d process support unit at 450°C under 17 MPa H<sub>2</sub> pressure, and an Australian brown (Morwell) coal were ground to pass 250  $\mu$  m screen and dried in vacuo for 10 hr at 100°C. Their elemental analyses are summarized in Table 1.

The ground coal was mixed with 10 vol% alcohol / 0.01 N or 1 N HCl, stirred for prescribed times under reflux or at room temperature, filtered, washed with water, and dried at 100°C for 10 hr.

Synthetic FeS<sub>2</sub> and commercially available KF-842 (Ni-Mo/Al<sub>2</sub>O<sub>3</sub>) catalysts were presulfided at 360°C for 6 hr before their use.

1,2,3,10b-tetrahydrofluoranthene (4HFL) was chosen as a liquefaction solvent because of reasons why it has high dissolving activity when dehydrogenated, high boiling point and thermal stability, and four donorable hydrogens in a molecule. 4HFL was prepared from fluoranthene by hydrogenation at 250°C under 15 MPa using the sulfided NiMo catalyst,<sup>7,8)</sup> followed by vacuum distillation and recrystallization procedure for its purifications.

Liquefaction was carried out in an autoclave (50 ml volume). The ground coal (3.0 g), the

solvent (4.5g) and catalyst (0.09g) were transferred to the autoclave. The products remaining in the autoclave were extracted with THF, benzene and hexane. The hexane soluble (HS), hexane insoluble but benzene soluble (HI-BS), benzene insoluble but THF soluble (BI-THFS), and THF insoluble (THFI) substances were defined as oil, asphaltene, preasphaltene, and residue, respectively. A small amount (<5%) of solvent derived products, which remained in the HI-BS fraction, was corrected by g.c. analysis. The gas yield was calculated by the difference between the initial (dry ash free base) and recovered residual weights. Thus, the weight loss during the experiment was included in the gas yield.

The first step in two-step liquefaction was carried out in a tube bomb of 20 ml capacity (the heating rate: ca.250°C/min) or autoclave of 50 ml capacity (ca.8°C/min). The coal (3 g) and the solvent (3 or 4.5 g) were transferred into the reactor, which was then pressurized with nitrogen to 1 MPa at room temperature after replacing the air with nitrogen. The tube bomb was then immersed in a molten tin bath at the prescribed temperature and agitated axially. The same procedure was applied to the autoclave liquefaction except for much slower heating rate in an electric furnace.

## RESULTS

### Effects of Deashing Pretreatment on the Liquefaction of Wandoan coal

Products distributions in the non-catalytic hydrogen-transferring liquefaction of Wandoan and its deashed coals are illustrated in Figure 1. 4HFL solvent of three times weight to the coal was very effective to liquefy the non-treated coal into 38% oil and 34% asphaltene by the reaction at 420 °C-30 min under 2 MPa N<sub>2</sub> pressure, leaving 18% preasphaltene and 6% residue. The deashing with 1 N HCl / 10% methanol at 60°C increased very much the oil yield upto 49% with decreased yields of asphaltene, preasphaltene, and residue. Especially, the reductions of asphaltene and residue yields are remarkable by deashing. These results suggest that the deashing pretreatment can accelerate the conversions of THFI residue containing some of inert macerals to soluble fractions, since the coal carries ca. 20 % of total unreactive macerals, as well as those of pre-asphaltene and asphaltene to oil.<sup>(10,11)</sup>

Figure 2 illustrates the products distributions in the catalytic liquefaction of Wandoan and its deashed coals at 450°C with FeS<sub>2</sub> catalyst under 15 MPa H<sub>2</sub> pressure. The liquefaction at 450°C -60 min and 4HFL/coal ratio of 1.5 converted 90% of the coal into soluble products with major products of 48% oil and 38% gas, leaving 9% of THFI residue. The deashing pretreatment at room temperature, regardless of the acid concentration, reduced the residue to 5%, although the enhanced yield of gas led to no increase of oil yield. It is noted that the deashing pretreatment even under much milder conditions with dilute acids can activate the coal, reducing the heavy liquefaction products probably by suppressing their retrogressive reactions.

Figure 3 illustrates the two-stage liquefaction of Wandoan and its deashed coals under reaction conditions of 450°C-7 min at the first step without catalyst and 400°C-20 min under 10 MPa H<sub>2</sub> pressure at the second step with FeS<sub>2</sub> catalyst. The deashing pretreatment at 60°C with 10% methanol/1 N HCl decreased the gas yield very much with 70% oil yield by the mixed solvent of 75% 4HFL / 25% pyrene at the solvent/coal ratio of 1.5, although the yields of heavy products were larger than those of the non-treated coal probably due to shortage of transferable hydrogens at the solvent/coal ratio of 1.5. Highly active catalysts for direct hydrocracking of asphaltene and pre-asphaltene and/or rehydrogenating dehydrogenated solvents are to be designed for further increase of distillate yield at the low solvent/ coal ratio of 1.5 under lower hydrogen pressure of 10 MPa.

### Influences of Deashing on the Liquefaction of Morwell coal

Effects of deashing time under reflux and at room temperature on the non-catalytic hydrogen-transfer liquefaction of Morwell coal are illustrated in Figures 4 and 5, respectively. The deashing under reflux for 24 hr gave inferior product distributions compared to those of the same treatment but for shorter treatment times, indicating that some retrogressive reactions should take place during the deashing under reflux. On the other hand, the deashing at room temperature for 24 hr provided

much better product distributions, giving 40% of oil yield and ca. 60% of oil+asphaltene yield.

Figure 6 shows the product distribution in the two-step liquefaction of deashed Morwell coal which was pretreated in 10% methanol/1 N HCl under reflux and at room temperature for 24 hr. The pretreatment at room temperature gave higher oil yield ca. 50% with less preasphaltene yield of 2% than those given by the deashing under reflux conditions. Thus, the complete conversion to oil and asphaltene, which can be fed to the second upgrading stage, can be achievable by the multi-stage liquefaction scheme.

#### Catalytic Upgrading of Wandoan liquefaction distillation residue(WD-LR)

Figure 7 shows products distributions in the catalytic upgrading of WD-CR produced in the I/d process support unit of NEDOL process. The WD-CR consists of 27% HS, 44% HI-BS, 11% BI-THFS, and 18% THFI. The single-stage hydrotreatment at 380°C-40 min with FeS<sub>2</sub> catalyst increased HS yield to 54%. The two-stage hydrotreatment, where the first stage was non-catalytic hydrogen transfer at 4HFL/CR of 1.5 at 450°C-7 min without catalyst followed by the second stage at 400°C-20 min with FeS<sub>2</sub> catalyst, further increased the HS yield to 71% with decreasing yields of BI-THFS and THFI to 2 and 3 %, respectively. However, a large amount (24 %) of HI-BS (asphaltene) still remained even after the two-stage hydrotreatment, indicating that the asphaltene fraction should suffer some retrogressive reactions during the PSU liquefaction process because of higher reaction temperature and/or excessive heating during the vacuum distillation of liquefaction products. Hence, multi-stage approaches are suggested to be designed to suppress the retrogressive reactions for the complete conversion of organic fractions into oil, because the refractory products are very difficult to be upgraded even in the catalytic process.

#### DISCUSSIONS

Current research on the coal macromolecules emphasizes their linearity in terms of their covalent bonds in their chain concerned, suggesting their high solubility in potential. The three dimensional networks of the macromolecules are principally formed by the non-covalent bridges through their chains to determine the properties and reactivity such as solubility and recombination of the thermally fissioned bonds as the solid or highly viscous state of the coal. Hence, the liberation of any non-covalent bridges prior to or during the liquefaction is expected to enhance the solubility of macromolecules and suppress the retrogressive reaction of produced radical species, favoring the progress of liquefaction. Such non-covalent bridges can be found in the asphaltene and preasphaltene which are substantially polymeric, carrying still a number of polar functional groups.

The reasons why the inert macerals are inert in the pyrolytic and liquefaction processes appear multi-fold. Many fusinites are believed to be like char, where a large condensed-aromatic planes have stacked in amorphous manners as if it had been carbonized. However, some of the inertinites consist of organic macromolecular chains strongly bound each other just like some thermosetting polymers such as cellulose. The latter structure can be liberated to be reactive by deshing treatment.

The present study revealed that acid washing to remove cationic ions enhanced the liquefaction to reduce the organic residue. By the acid of solvent of hydrogen donor and dissolving ability, no THF insoluble organic residue is left after the liquefaction of some coals, especially for Australian brown coals.<sup>(1)</sup> The present study revealed that the deashing pretreatments can accelerate the depolymerization of Wandoan subbituminous coal, converting it almost completely to THF soluble fraction even though it has a large amount of inert macerals.<sup>(2)</sup> Such pretreatments significantly reduced the amount from coals which carry a significant amount of inert macerals. Some of inert macerals are activated to be liquefied by the treatment. The acid treatment is also effective to activate asphaltene and preasphaltene by removing trace amount of cationic ions. Such all results indicate major roles of cationic bridges in the coal macromolecules which are one of the major obstacles for their smooth depolymerization.

Other pretreatments such as preheattreatment<sup>(3)</sup> and impregnation of polar reagent<sup>(4)</sup> are

also effective, although their significance is not fully proved. Although more effective conditions or procedures should be explored, the principles to liberate macromolecular assemblies appear correct. The intermolecular bridges are postulated as hydrogen bonds, cationic bridges, charge transferring polar bonds, and  $\pi - \pi$  stacking. Such bridges except for the last one in the high ranking coals are based on the polar groups. Hence, any procedures to remove polar groups and to loosen their non-covalent interactions can be effective. The recombination reactions should be carefully avoided when the polar groups are intended to be removed. The conditions should be carefully controlled.

Selection of solvent in terms of hydrogen donor and dissolving ability as well as optimization of liquefaction conditions in terms of heating rate, temperature and time are carefully designed<sup>15)</sup>, since the progressive and retrogressive reactions always take place competitively and consecutively in the coal liquefaction. The change of solvent according to the reaction progress should be also taken into account. The optimum conditions for the catalysis under high hydrogen pressure may differ from those of non-catalytic thermal process.<sup>16)</sup> Hence, the multi-stages are very reasonable to set up the optimum conditions from the respective stages. Although we have not yet reached to clarify the optimum conditions, we have achieved the highest yields of oil and asphaltene with least amount of organic residue.

The present authors have proposed two types of recoverable catalysts for the coal liquefaction.<sup>11)</sup> They are separable by their stable ferromagnetism under coal liquefaction conditions and by floating ability to the boundary layer of two solvents. Preliminary results may promise their recovery and catalytic activities. The deashing pretreatment facilitate the recovery and regeneration of the catalyst for its repeated uses.<sup>17)</sup> Further development is now in progress.

## REFERENCES

- 1) Mochida, I., Sakanishi, K., Sakata, R., Honda, K., Umezawa, T., *Energy & Fuels* in press.
- 2) Mochida, I., Yufu, A., Sakanishi, K., Korai, Y., *Fuel*, 1988, 67, 114.
- 3) Larsen, J.W., Pan, C.-S., Shawver, S., *Energy & Fuels*, 1989, 3, 557.
- 4) Sakanishi, K., Honda, K., Mochida, I., Okuma, O., *Proc. Pittsburgh Coal Conf.*, 1993, 198.
- 5) Mochida, I., Takayama, A., Sakata, R., Sakanishi, K., *Energy & Fuels*, 1990, 4, 81.
- 6) Sakata, R., Takayama, A., Sakanishi, K., Mochida, I., *Energy & Fuels*, 1990, 4, 585.
- 7) Mochida, I., Otani, K., Korai, Y., *Fuel*, 1985, 64, 906.
- 8) Mochida, I., Kawamoto, N., Kishino, M., Otani, K., Korai, Y., *Fuel*, 1986, 65, 81.
- 9) Mochida, I., Sakanishi, K., Kishino, M., Honda, K., Umezawa, T., Yoon, S.H., *ACS Div. Fuel Chem.*, 1993(Denver), 38(1), 93.
- 10) Mochida, I., Kishino, M., Korai, Y., Sakanishi, K., *J. Fuel Soc. Jpn.*, 1986, 65, 828.
- 11) Mochida, I., Yufu, A., Sakanishi, K., Zhao, X.Z., Okuma, O., Hirano, T., *J. Fuel Soc. Jpn.*, 1989, 68, 244.
- 12) Mochida, I., Kishino, M., Sakanishi, K., Korai, Y., Takahashi, R., *Energy & Fuels*, 1987, 1, 343.
- 13) Mochida, I., Yufu, A., Sakanishi, K., Korai, Y., Shimohara, T., *J. Fuel Soc. Jpn.*, 1986, 65, 1020.
- 14) Korai, Y., Torinari, Y., Mochida, I., *Cokes-circular Jpn.*, 1992, 41(4), 232.
- 15) Mochida, I., Sakanishi, K., Korai, Y., Fujitsu, H., *Fuel Process. Technol.*, 1986, 14, 113.
- 16) Sakata, R., Sakanishi, K., Mochida, I., *Proc. Int. Conf. Coal Sci.*, 1991, 707.
- 17) Sakanishi, K., Honda, K., Sakata, R., Mochida, I., *5th Australian Coal Sci.*, 1992, 97.

Table 1 Elemental Analyses of Coals and Liquefaction Residue

	Wt % (d.a.f. basis)				Ash (Wt %)
	C	H	N	(O+S)diff.	
Wandoan coal	76.3	6.1	1.1	16.5	7.9
Deashed Wandoan coal	76.2	6.2	1.0	16.6	7.0
Wandoan-PSU residue	85.8	5.6	1.5	7.1	29.4
Morwell coal	66.7	4.9	0.6	27.8	2.3
Deashed Morwell coal	63.4	5.0	0.6	31.0	1.7

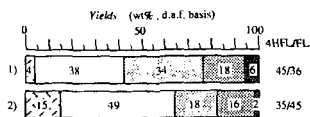


Figure 1 Effect of deashing on the hydrogen-transfer liquefaction yield from Wandoan coal

1): non-treated Wandoan coal,  
2): Deashed Wandoan coal under reflux in 10wt% MeOH/1N HCl for 24hr  
(liquefaction conditions 4HFL/coal=9.0/3.0g, 20 atm N<sub>2</sub>, 420°C-30min)

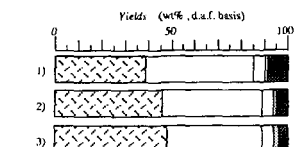


Figure 2 Effect of deashing on the catalytic liquefaction yield from Wandoan coal

Legend: Gas, Oil, Asphaltene, Preasphaltene, THFI  
coal pretreatment conditions:  
1) non-treated Wandoan coal  
2) 1N-HCl/10wt% EtOH / room temperature / 6hr  
3) 0.01N-HCl/10wt% EtOH / room temperature / 6hr  
liquefaction conditions (catalytic liquefaction):  
4HFL/coal/FeS<sub>2</sub> catalyst = 5/3.00/0.09(g)  
H<sub>2</sub> reaction pressure=15 MPa, 450°C-60 min

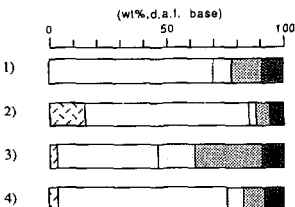


Figure 3 Influence of deashing on the two-stage liquefaction of Wandoan coal

(4HFL/Pyrene/Coal = 3.4/1.1/3.0 g)

Legend: Gas, Oil, Asphaltene, Preasphaltene, THFI

1),2): non-treated coal,  
3),4): deashed coal under reflux in 10% MeOH/1N HCl  
1) Non-catalytic first stage at 450°C-7 min  
2) Catalytic second stage at 400°C-20 min  
3) Non-catalytic first stage at 450°C-7 min  
4) Catalytic second stage at 400°C-20 min

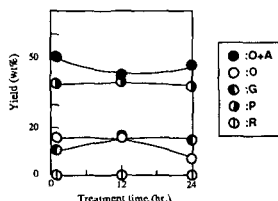


Figure 4 Effect of deashing time under reflux on the liquefaction yield from Morwell coal

(Deashing treatment: under reflux in 10% MeOH/1N HCl)

(430°C-2min., 4HFL/coal=1.5/1, no catalyst, 20 atm N<sub>2</sub>, tube bomb)

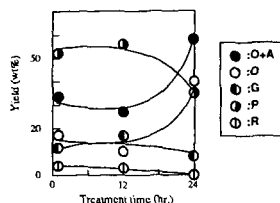


Figure 5 Effect of deashing time at room temperature on the liquefaction yield from Morwell coal

(Deashing treatment: at room temperature, 10% MeOH/1N HCl)

(430°C-2min., 4HFL/coal=1.5/1, no catalyst, 20 atm N<sub>2</sub>, tube bomb)

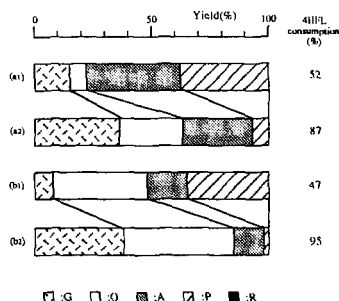


Figure 6 Two-stage liquefaction of deashed Morwell coal

(a1),(b1) First-stage Non-catalytic Hydrogen-transferred Morwell Coal in the Two-stage Hydro-treatment (430°C-2min, 20 atm N<sub>2</sub>, tube bomb and molten tin bath, rapid heating)

(a2),(b2) Second-stage Catalytic Hydrothermal Morwell Coal in the Two-stage Hydro-treatment (380°C-20 min, 50 cc autoclave, slow heating)

(a1),(a2) Deashing treatment: under reflux, 24hr, 10% MeOH/1N HCl

(b1),(b2) Deashing treatment: room temp., 24hr, 10% MeOH/1N HCl

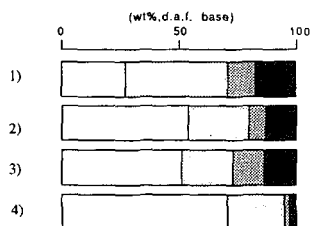


Figure 7 Single- and two-stage hydrotreatments of Wandoan liquefaction residue (WD-LR)

Legend: Oil, Asphaltene, Preasphaltene, THFI

1) WD-LR as received  
2) Single-stage hydrotreatment at 380°C-40 min (autoclave) under 10 MPa H<sub>2</sub> with FeS<sub>2</sub> and 75% 4HFL/25% pyrene at solvent/WD-LR of 1.5  
3,4): Two-stage hydrotreatment;  
3) Non-catalytic first-stage hydrotreatment at 450°C-7 min (rapid heating) under 2 MPa N<sub>2</sub> with 75% 4HFL/25% pyrene at solvent/WD-LR of 1.5  
4) Catalytic second-stage hydrotreatment at 400°C-20 min (autoclave) under 10 MPa H<sub>2</sub> with FeS<sub>2</sub>